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(54) Electret

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Examiner: H. Oda

(57) Claims

1. An electret comprised of 4-methyl-1-pentene and at least one compound selected from

(a) a compound containing phenol hydroxyl group;

(b) higher aliphatic carboxylic acid and its metal salts;

(c) thiocarboxylate compound;

(d) phosphorous compound, and

(e) ester compound.

Detailed Explanation of the Invention

This invention pertains to electrets with long-term stability. Electrets are widely applied in various field. Polymers such as polyethylenes and polypropylenes have been a likely candidates for electret materials. However, the materials lack stability since the damping effect progresses quickly in these materials.

The objective of this invention is to produce an electret with superior long-term stability.

4-methyl-1-pentene polymer used in this invention is mono polymer, or copolymer of 4-methyl-1-pentene and other α -olefins such as 1-butene, 3-methyl-1-butene, 1-pentene, 1-hexene, 3-methyl-1-pentene, 1-octene, 1-decene, 1-tetradecene, and 1-octadecene. In this case, a copolymer comprised of 4-methyl-1-pentene and C₆ - C₁₈ α -olefin is especially desirable. The amount of the said α -olefin in the copolymer is 0.3 - 20 mol%, preferably 1 - 12 mol%.

The said copolymer may contain vinyl monomers containing double bonds in the molecule.

Concrete examples of vinyl monomers are: maleic acid anhydride, citraconic acid anhydride, itaconic acid anhydride, 5-norbornane-2,3-dicarboxylic acid anhydride, tetra-hydro phthalic acid anhydride, methyl acrylate, ethyl acrylate, methyl methacrylate, butyl acrylate, glycidyl acrylate, glycidyl methacrylate, mono-ethylene maleate, diethylene maleate, acryl amide, maleic acid monoamide, maleic acid diamide, maleic

acid-N-monoethyl amide, maleic acid N, N-diethyl amide, maleic acid N-monobutyl amide, maleic acid N,N-dibutyl amide, monoamide fumarate, diamide fumarate, fumaric acid N-monoethyl amide, fumaric acid N, N-diethyl amide, fumaric acid N-monobutyl amide, fumaric acid N,N-dibutyl amide, maleimide, N-butyl maleimide, N-phenyl maleimide, acrylic acid 2-hydroxyethyl, acrylic acid 2-hydroxypropyl, N,N'-dimethyl aminoethyl methacrylate, acryl amide, and sodium acrylate. Monomers such as acrylonitrile, 4-vinylpyridine, styrene, and vinyl acetate can also be mentioned.

4-methyl-1-pentene can be denatured by known methods with the above monomers. The monomer concentration level in the

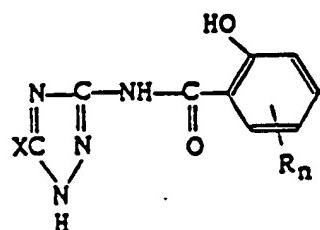
polymer is 10^{-4} - 100 wt%, preferably 10^{-2} - 10 wt%.

The following compounds may be added to 4-methyl-1-pentene:

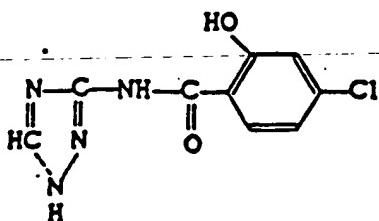
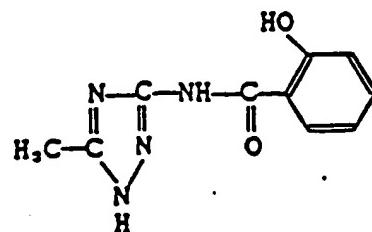
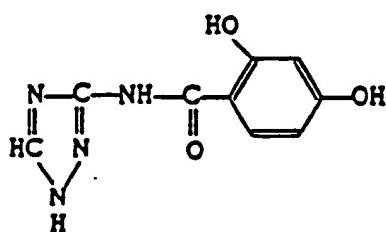
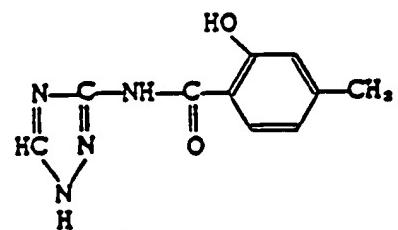
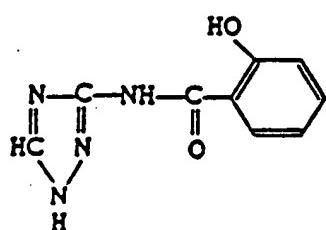
(a) Compounds containing phenol hydroxyl group:
2,6-di-tert-butyl-p-cresol (BHT), 2,6-di-tert-butylphenol, 2,4-
dimethyl-6-tert-butylphenol, 2-methyl-4,6-di-nonylphenol,
butyl-hydroxy anisole, styrenated phenyl, 2,4,6-tri-tert-butyl
phenol, n-octadecyl-3-(4'-hydroxy-3',5'-di-tert-butylphenol)
propionate; 4,4-dihydroxy diphenyl, 2,2'-methylene bis(4-methyl-
6-tert-butylphenol), 2,2'-methylene bis(4-ethyl-6-tert-butyl
phenol), 2,2'-methylene bis(4-methyl-6-cyclohexyl phenol),
4,4'-methylene bis(2,6-di-tert-butyl phenol), 4,4'-butyldiene
bis(3-methyl-6-tert-butyl phenol), 1,1-bis(4-hydroxy phenyl)
bis(cyclohexane, 2,2'-dihydroxy-3,3'-di-(α -methyl cyclohexyl)-5,5'-
dimethyl-diphenylmethane, 1,3,5-trimethyl-2,4,6-tris(3,5-di-tert-
butyl-4-hydroxy benzyl)benzene, tris(2-methyl-4-hydroxy-5-tert-

butylphenyl)butane, tetrakis[methylene-3-(3',5'-di-tert-butyl-4'-hydroxyphenyl)propionate]methane (Irganox 1010),
 4,4'-thiobis (6-tert-butyl-3-methylphenol),
 4,4'-thiobis (6-tert-butyl-o-cresol),
 2,2'-thiobis(6-tert-butyl-4-methylphenol)2,5-di-tert-butyl hydroquinone, hydroquinone-monomethyl ether, and
 2,5-di-(tert-amyl)hydroquinone.

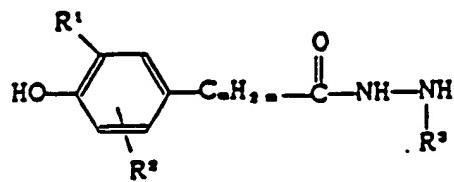
Furthermore, triazol compounds shown in the formula below



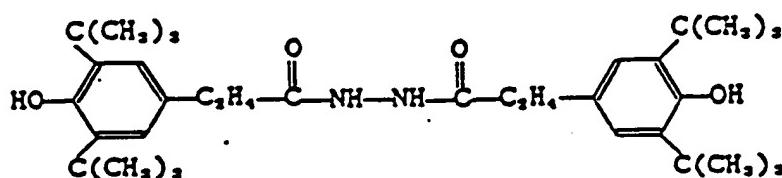
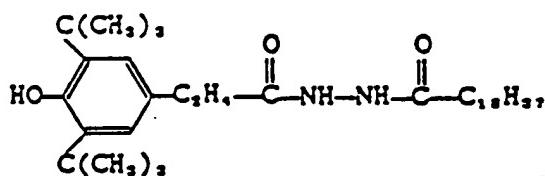
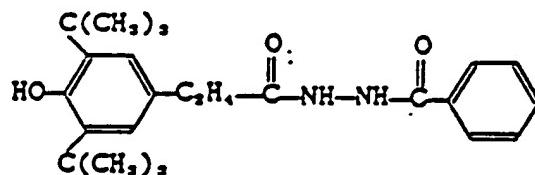
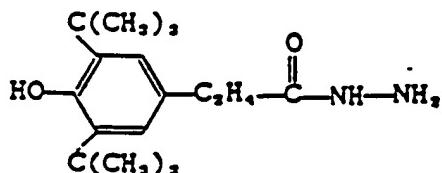
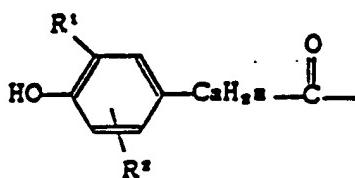
(X is H or Cl-C18 alkyls, R is Cl-C18 alkyls, hydroxyls, or halogens. $0 \leq n \leq 3$, R may be the same or different)
 can be mentioned, and examples are:



Also, hydrazine compounds shown in the formula below:



(R¹ is C1-C12 alkyls, R² is H or C1-C12 alkyls, R³ is H, C2-C18 alkanoyl, or radicals shown in 0≤m≤5), and examples are:



Among the said phenol hydroxyl containing compounds, compounds containing tert-butyl are desirable.

(b) Higher aliphatic carboxylic acid compounds

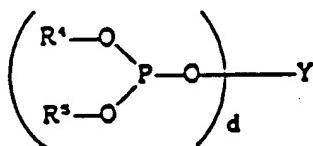
Lauric acid, palmitic acid, stearic acid, behenic acid, and their salts.

(c) Thiocarboxylate compounds

di-lauryl-thio-di-propionate, di-stearyl-thio-di-propionate, lauryl-stearyl-thio-di-propionate, di-myristyl-thio-di-propionate, di-tridecyl-thio-di-propionate, and penta-erythritol-tetra(dodecyl thio-propionate).

(d) Phosphorous compounds

Triphenyl phosphite, tricresyl phosphite, tridecyl phosphite, trioctadecyl phosphite, tri(tert-octylphenyl) phosphite, tri(tert-nonylphenyl)phosphite, phenyl-di(2-ethylhexyl)phosphite, and compounds shown in general formula:

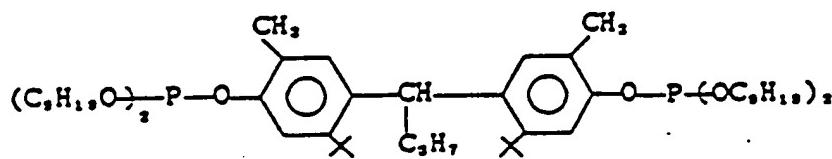
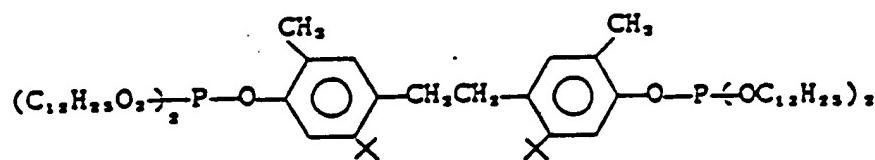
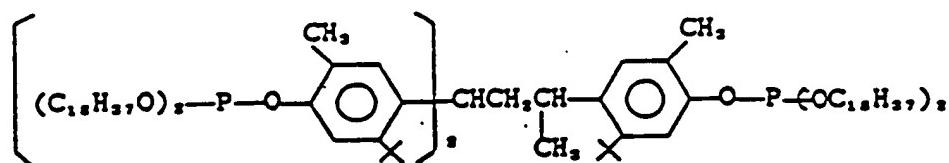


(R⁴ and R⁵ are organic radicals with C1-C80 selected from alkyls, alkenyls, aryls, and cycloalkyls, d is 1 - 4).

In the said compound, Y is 4,4'-dihydroxy diphenyl, 2,2'-methylen bis(4-methyl-6-tert-butylphenol), 4,4'-methylene bis(2,6-di-tert-butylphenol), bisphenol A, alkylated bisphenol,

1,3,5-trimethyl-2,4-6-tris(3,5-di-tert-butyl-4-hydroxy benzyl) benzene, or tris(1-methyl-4-hydroxy-5-tert-butyl benzyl)1,1,3-butene.

For R⁴ and R⁵, higher alkyls with C9 or above are desirable. In this case, di-stearyl pentaerithritol di-phosphite and compounds shown below:



In the compounds, + is tert-butyl.

(e) Ester compounds

Compounds with ester bonds, such as Irguranox 1010, can be mentioned.

The weight composition of one or a combination of the above described compounds (a) - (e) is 10^{-2} - 100 parts for 100 parts polymer, and 10^{-2} - 10 parts is preferred.

The polymer may contain compounds such as carnauba wax, polyethylene wax, polybutene, polyamide, polyester, polycarbonate, ionomer, polyvinyl acetate, polystyrene, ABS resin, acrylic resin, vinyl chloride, petro resin, rosin, natural rubber, fluorine resin, and epoxy resin. Furthermore, regular additives such as processed oil, plasticizers, dyes, pigments, and stabilizers may also be contained.

The electret of this invention is formed into fibers, films, tubes, and porous films by conventional means.

The electret of this invention displays a long-term storage stability and can be suitably used for acoustic elements, filters, memory elements, and in medical fields.

The invention is further explained with examples.

Practical Example 1

0.1 wt% BHT was blended with poly-4-methyl-1-pentene powder with a molecular weight of 300,000 and formed into a film at 300°C.

The film was placed between electrodes, and DC -10KV was applied, heat-treated for 2 minutes at 120°C, cooled to room temperature, and the charge was discontinued.

The surface potential of the electret obtained was 4100 V. The electret was stored at 25°C, 60 - 70 %RH for 7 days and when the potential was checked again, the value obtained was -3300 V.

The surface potential was checked by a rotational sector type surface voltmeter.

Practical Examples 2 - 8

In practical example 1, compounds shown in table 1 were used. The results are shown in the table.

(1) Compounds

| | |
|---------|---------------------------------------|
| P. ex 2 | Zinc stearate |
| P. ex 3 | Iruganox 1010 |
| P. ex 4 | Lauryl·stearyl·thiopropionate |
| P. ex 5 | Tri(t-nonylphenyl)phosphite |
| P. ex 6 | Iruganox 1010 Zinc stearate |
| P. ex 7 | BHT Calcium stearate |
| P. ex 8 | Iruganox 1010 BHT Zinc stearate |

(2) Wt Composition (wt%)

(3) Static charge

- (a) Right after application
- (b) After 7 days

| Example | (1) 化合物 | (2) 配合量 (重量%) | (3) 静電圧(静電ボルト) | |
|---------|----------------------------------|-------------------|----------------|-------|
| | | | 印加直後 | 7日経過後 |
| 実施例2 | ステアリン酸亜鉛 | 0.5 | -4200 | -3500 |
| " 3 | イルガノツクス 1010 | 0.2 | -3600 | -2000 |
| " 4 | ラウリル・ステアリル チオジプロピオネート | 0.3 | -4000 | -3000 |
| " 5 | トリ(イーノニルフェニル) ホスフアイト | 0.5 | -3700 | -1500 |
| " 6 | {イルガノツクス 1010 ステアリン酸亜鉛 | 0.2 0.5 | -4000 | -3600 |
| " 7 | {BHT ステアリン酸カリシウム | 0.1 0.1 | -4300 | -3500 |
| " 8 | {イルガノツクス 1010 BHT ステアリン酸亜鉛 | 0.2 0.1 0.5 | -3900 | -3000 |

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